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(54) CRYSTALLINE ZEOLITIC ALUMINOSILICATE CRACKING
 CATALYST COMPOSITION IN FORM OF MICROSPHERES
 AND PREPARATION THEREOF

(71) We, ENGELHARD MINERALS & CHEMICALS CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, located at Menlo Park, Edison, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a cracking catalyst composition containing synthetic crystalline faujasite, the catalyst being in the form of small essentially spherical particles (microspheres) suitable for use in a fluid bed process for converting gas-oil feedstock to gasoline. The invention relates also to the preparation of the catalyst from preformed silica-alumina microspheres containing calcined kaolin clay.

Catalysts for fluid hydrocarbon conversion processes, e.g., cracking catalysts, are frequently supplied in the form of very small essentially spherical particles predominantly within the range of 100/325 mesh (Tyler). These particles are usually called "microspheres." The microspheres must possess certain properties among which is hardness, especially resistance to attrition. The particles must also possess adequate activity and selectivity as well as thermal and steam stability.

Highly active and selective cracking catalysts have been prepared by incorporating finely divided crystals of certain crystalline zeolitic aluminosilicates of the molecular sieve type with suitable matrix material such as clay or silica-alumina gels. Ion-exchanged synthetic faujasite (zeolite X or Zeolite Y) is a suitable crystalline zeolite.

Faujasite may be synthesized from dilute high purity sources of Na_2O , Al_2O_3 and SiO_2 . It may also be synthesized by reacting sodium hydroxide solution with calcined

kaolin clay. However, in order to obtain faujasite, rather than other zeolitic molecular sieves, the clay must be calcined at relatively high temperature and undergo the characteristic kaolin exotherm. The incorporation of small amounts of kaolin clay calcined at lower temperature ("metakaolin") may aid in the crystallization of the faujasite but, when used as the sole source of silica and alumina, metakaolin does not result in the crystallization of faujasite.

Microspherical zeolitic cracking catalyst particles have been obtained by forming a slurry of previously formed powdered zeolite crystal with dilute silica hydrosol or alumina-silica hydrosol and spray drying the slurry. Catalyst particles obtained by such processing are expensive since expensive high purity materials are required to prepare the zeolite and a separate binding step is required. The attrition resistance of the products obtained by binding sieve crystals generally leaves something to be desired.

Attempts have also been made to form zeolitic molecular sieve compositions from preformed bodies of essentially the same size and shape as the finished catalyst particles. This has been successfully accomplished by extruding a mixture of caustic solution and clay material, part of which is anhydrous and calcined and part of which is hydrated. The extruded pellets, generally in the shape of cylindrical pellets, are subjected to hydrothermal treatment without dehydration. Faujasite crystallizes in situ in the presence of hydrated kaolin clay as a result of the reaction between the caustic and the calcined clay in the pellets. A feature of the process is that reaction and crystallization are carried out in the absence of an external aqueous phase in contact with the pellets. Thus, there is no extraction of constituents of the pellets. The ultimate catalyst product obtained by ion-exchange

ing and activating the crystallized product has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of about 2/1 — i.e., essentially the same ratio that is present in kaolin clay.

5 Great difficulty has been experienced in preparing crystalline zeolitic molecular sieve composite catalysts in the form of microspheres by the in situ process above described. Problems have been encountered in
10 obtaining discrete microspheres and in crystallizing faujasite from preformed particles containing caustic solution and a mixture of calcined and hydrated kaolin clay. Especial difficulty has been encountered in obtaining
15 small spherical particles having the desired resistance to attrition. One reason for the difficulties is that when faujasite is crystallized in situ in the presence of hydrated kaolin in microspherical preforms the small
20 spheres tend to agglomerate and stick to each other during reaction and crystallization. On the other hand, impregnation of caustic solution into preformed microspheres composed of the mixture of hydrated and calcined clay tends to result in
25 the mechanical breakdown of the preforms unless great care is exercised. When caustic is included in the feed to the spray dryer so that it is present in the preformed microspheres, part of the caustic tends to react
30 with combustion gases in the spray dryer and difficulty is experienced crystallizing the zeolite.

We have now devised a simple method
35 for making a microspherical crystalline zeolitic molecular sieve catalyst of superior hardness from preformed bodies and at a low cost, containing a desired zeolitic molecular sieve as a constituent.

40 One aspect of this invention provides a cracking catalyst in the form of attrition-resistant microspheres comprising ion-exchanged synthetic crystalline faujasite and the porous amorphous silica-alumina residue of calcined kaolin clay obtained when
45 the sodium form of faujasite was crystallized in situ by hydrothermal treatment with agitation at 150°-200°F of a suspension in a dilute sodium hydroxide solution of amorphous silica-alumina microspheres comprising
50 calcined kaolin clay, said calcined clay having undergone the kaolin exotherm during calcination.

Preferably the catalyst analyses (on a
55 volatile-free weight basis) less than 1% Na_2O , from 30% to 50% SiO_2 and from 50% to 65% Al_2O_3 , the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the faujasite constituent being in excess of 4.0.

60 The NH_4^+ -exchanged form of the catalyst of the invention, after thermal activation, is eminently suitable for use in cracking gas-oil feed-stock to produce gasoline. The product possesses high selectivity towards
65 gasoline with low coke production and it

operates at a high level of activity. It has outstanding resistance to deterioration by high temperature steam.

A further aspect of the invention provides a process for preparing the catalyst
70 defined above which comprises spray drying a slurry in water of hydrated kaolin clay or a mixture of hydrated and calcined kaolin clay to form microspheres, calcining the microspheres until the hydrated
75 kaolin clay is dehydrated and the microspheres at least partially undergo the kaolin exotherm, suspending said microspheres in an aqueous solution of an alkali metal hydroxide, maintaining said microspheres in
80 said aqueous solution at a temperature of 65° to 130°F, subsequently agitating said microspheres in said solution at a temperature of 150° to 200°F until hydrated alkali
85 metal faujasite crystals form in said microspheres, and silica is leached therefrom, separating the microspheres from said aqueous solution and ion-exchanging said
90 microspheres to reduce the alkali metal content thereof.

According to one embodiment of this process one proceeds by spray drying an aqueous slurry of kaolin clay at least 50%
95 by weight of which is hydrated, thereby forming small essentially spherical particles, calcining said particles until any hydrated kaolin clay is dehydrated and the particles undergo the exothermic reaction which is characteristic of kaolin clay, incorporating
100 the calcined particles with alkali metal hydroxide solution to form a fluid slurry, maintaining said fluid slurry at a temperature of 65° to 130°F, subsequently agitating said spherical particles at a temperature of
105 150° to 200°F and maintaining sufficient water to keep the slurry fluid until silica is extracted from the particles and crystalline alkali metal faujasite is present in the particles, separating the particles from the
110 mother liquid containing dissolved alkali metal silicate, and ion-exchanging the crystallized particles to reduce the alkali metal content.

Another process for making the catalyst
115 of this invention comprises reacting meta-kaolin in the form of calcined coherent first microspheres substantially free from hydrated kaolin clay and calcined kaolin clay that has undergone the exotherm
120 in the form of calcined second microspheres substantially free from meta-kaolin and hydrated kaolin clay, with sufficient sodium hydroxide solution to form a fluid slurry, and carrying out hydrothermal
125 treatment by maintaining said fluid slurry at a temperature of 65° to 130°F, subsequently heating at a temperature of 150° to 200°F while agitating said fluid slurry sufficiently to keep the microspheres in suspension,
130 and separating the microspheres

containing crystalline sodium faujasite-type zeolite and amorphous alumina-silica from the aqueous phase of the slurry.

The microspherical catalyst may thus be prepared by mixing hydrated kaolin clay (or a mixture of hydrated and calcined clay) in water, spray drying the mixture to form microspheres, calcining the microspheres until the hydrated kaolin clay is dehydrated and the microspheres undergo or pass through the characteristic kaolin exotherm. As a result of calcination under such conditions, essentially all of the clay is dehydrated and put into a state or condition such that a portion of it will react with sodium hydroxide solution to form crystalline faujasite. Simultaneously, the microspheres become remarkably attrition-resistant and certain difficulties encountered in crystallizing the faujasite from preformed microspheres containing hydrated clay are obviated. The calcined silica-alumina microspheres are suspended in an aqueous solution of an alkali metal hydroxide, especially sodium hydroxide and, while the aqueous suspension is agitated, it is maintained first at mild temperatures and then at more elevated temperature, until hydrated alkali metal faujasite crystals form in the microspheres as a result of reaction between the aqueous reaction liquid and alumina and silica in the microspheres. During the hydrothermal treatment silica is leached from the microspheres, forming an alkali metal silicate mother liquid from which the crystallized microspheres are separated. After separation from the mother liquid the microspheres are ion-exchanged to reduce the alkali-metal content. Before or during use the microspheres are activated by heat treatment.

The method of the invention thus features the crystallization in situ of faujasite in preformed attrition-resistant silica-alumina microspheres of calcined kaolin clay free from hydrated kaolin clay by reaction of the microspheres in an aqueous reaction liquid which leaches silica from the microspheres before crystallization is completed. Such method differs from the prior art method of making a composite zeolitic catalyst which features the reaction between caustic solution and calcined clay in situ in the presence of hydrated kaolin clay, the caustic being present in the original preforms and the reaction being carried out without leaching of constituents of the preforms.

In an embodiment of the invention meta-kaolin is also incorporated in the reaction liquid, the metakaolin being incorporated in the form of particles separate from the microspherical particles which were calcined at elevated temperature (the latter being referred to hereinafter as "Micro-

spheres A"). The metakaolin may be added as a powder or as calcined microspheres ("Microspheres B") obtained by calcining a portion of the same or similar spray dried microspheres used to obtain "Microspheres A" under milder calcination conditions. Thus, "Microspheres B" may be obtained by calcining spray dried hydrated kaolin clay until the hydrated kaolin dehydrates and undergoes an endothermic reaction associated with loss of water, the temperature and time being insufficient to cause the clay to undergo the characteristic kaolin exotherm.

A. Basic Process

"Microspheres A" are obtained by suitable calcination treatment of hydrated microspheres prepared by spray drying an aqueous slip of hydrated (uncalcined) kaolin clay or a mixture of hydrated kaolin clay with amorphous kaolin clay calcined at a temperature within the range of 1000°F. to 2200°F. Low-iron, high purity hydrated and calcined kaolins are preferred and are employed as fine (minus 325 mesh Tyler) particles. Fine particle size plastic hydrated clay is recommended.

When calcining clay at elevated temperature, e.g., temperature appreciably above 1800°F., the duration of the calcination should be limited to avoid the formation of new crystalline phases. The calcined clay should be amorphous when tested by standard X-ray diffraction although diffraction maxima characteristic of crystalline impurities such as anatase may be present. In other words, the calcined clay should produce an X-ray diffraction pattern free from strong peaks characteristic of high temperature alumina, silica or aluminum silicate crystalline phases.

The term "kaolin clay" as used herein embraces clays, the predominating mineral constituent of which is kaolinite, halloysite, nacrite, dickite, anauxite and mixtures thereof.

Suggested proportions are from 0 to 200 parts by weight calcined kaolin clay (moisture-free basis) to 100 parts by weight of raw, hydrated kaolin.

To facilitate spray drying, the powdered hydrated clay (or mixture thereof with calcined clay) is preferably dispersed in water in the presence of a small amount of a deflocculating agent exemplified by sodium silicate or a sodium condensed phosphate salt such as tetrasodium pyrophosphate. By employing a deflocculating agent, spray drying may be carried out at high solids levels and harder products are usually obtained. When a deflocculating agent is employed, slurries containing about 55% to 60% solids may be prepared. These high solids slurries are preferred to the 40% to 50% slurries

which do not contain a deflocculating agent. Higher solids slurry may also be prepared when all of the clay is in hydrated (uncalcined) condition. Thus, the use of hydrated kaolin clay as the sole clay material in combination with the use of deflocculating agent is especially preferred.

Other ingredients such as, for example, combustible fillers, may also be present in the slurry.

Several procedures can be followed in mixing the ingredients to form the slurry. One procedure, by way of example, is to dry blend the finely divided solids, add the water and then incorporate the deflocculating agent. The components can be mechanically worked together or individually to produce slurries of desired viscosity characteristics.

Spray dryers with countercurrent, cocurrent or mixed countercurrent and cocurrent flow of slurry and hot air can be employed to produce the microspheres. The air may be heated electrically or by other indirect means. Combustion gases obtained by burning hydrocarbon fuel in air can be used.

Spray drying results in the evaporation of water from droplets of the slurry and the formation of microspheres. Microspheres about 20 to 150 microns in equivalent spherical diameter are desired for most catalytic operations using fluidized contact masses.

Using a cocurrent dryer, air inlet temperatures to 1200°F. may be used when the clay feed is charged at a rate sufficient to produce an air outlet temperature within the range of 250°F. to 600°F. At these temperatures, free moisture is removed from the slurry without removing water of hydration (water of crystallization) from the raw clay ingredient. Dehydration of some or all of the raw clay during spray drying is, however, within the scope of the invention. The spray dryer discharge may be fractionated to recover microspheres of desired particle size.

To provide "microspheres A", the spray dried microspheres, or a desired size fraction of the microspheres, are calcined in an atmosphere having a temperature of 1600°F. to 2200°F., preferably from 1750°F. to 1850°F. and for a time (which will vary with calcination temperature) which results in calcined microspheres which do not exhibit a substantial exothermic peak at about 1800°F. when tested by standard differential thermal analysis (DTA). In other words, the microspheres are calcined under conditions such that any clay which has not undergone the kaolin exotherm before calcination, partially undergoes or passes through the exotherm after the microspheres have been formed. Preferably, the clay material

in the calcined microspheres should not have passed completely through the exotherm during heat treatment since difficulty may be experienced in crystallizing the desired zeolite when the clay is in this condition. At temperatures of 1600°F. prolonged calcination may be required. At temperatures of 2200°F. the calcination period must be of limited duration to avoid overcalcination.

The kaolin endotherm and exotherm can be readily determined by differential thermal analysis (DTA), using the technique described in Ralph E. Grim's "CLAY MINERALOGY," page 203, published by McGraw Hill Book Company, Inc. (1953).

At this point of the process, the microspheres are amorphous to X-rays except that peaks characteristic of crystalline impurities such as anatase may be present in X-ray diffraction patterns.

The microspheres are reacted with an aqueous alkaline liquid in which they are suspended, the liquid having a composition predetermined to result in the crystallization of a desired percentage of faujasite zeolite molecular sieve. Only a portion of the constituents of the calcined microspheres reacts to form the zeolitic molecular sieve and thus a composite of crystalline sieve and an amorphous residue is present in the crystallized microspheres. Generally speaking, after crystallization the microspheres should contain above about 15% crystalline faujasite-type zeolite, most preferably above 20% zeolite. The term "faujasite-type zeolite" embraces zeolite X and zeolite Y. Preferably a high silica form of sodium Y is crystallized, especially sodium zeolite Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in excess of 4.0. X-ray diffraction techniques may be used to estimate zeolite quantity, distinguish zeolite X from zeolite Y and determine the silica-to-alumina molar ratios of zeolite Y.

The aqueous alkaline solution must be employed in amount adequate to form a suspension sufficiently fluid to be stirred and containing sufficient Na_2O (or equivalent alkali metal oxide) at an operable concentration to crystallize the faujasite zeolite. Sodium hydroxide solutions of 12% to 22% concentration (w/w) are recommended. Solutions of 13% to 15% concentration are preferred. Sufficient solution may be used to provide from about 0.5 to 1.0 moles Na_2O per mole Al_2O_3 in the microspheres. When the concentration of Na_2O in the treating liquid is too low, the zeolite may not crystallize. When the concentration is too high, there may be insufficient liquid to produce a fluid suspension without employing a $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio that is excessively high and results in a zeolite hav-

ing an undesirably low $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

The microspheres are reacted with the sodium hydroxide solution in which they are immersed, preferably while the suspension is agitated, and maintained at a temperature within the range of 65°F. to 130°F. Crystallization does not take place during this phase of the hydrothermal treatment. Excellent results have been obtained at a temperature of 100°F. for 16 hours.

To crystallize the zeolite, the temperature of the suspension is increased to 150°F. to 200°F., usually for about 10 to 24 hours. During the crystallization, means should be provided to prevent substantial change in concentration due to loss of water from the system. This may be done, for example, by using a closed reactor, by providing the reactor with a water-cooled jacket to condense water that evaporates, by covering the aqueous suspension with a layer of oil or, when evaporating in an open reactor, by adding water to replace that lost by evaporation. When using oil to control evaporation, the impeller used to agitate the system should be well below the oil layer in order to maintain the oil as a distinct upper layer.

A feature of the process is that the hydrothermal treatment is terminated after substantially the maximum amount of synthetic faujasite has crystallized. If hydrothermal treatment is continued after this takes place, zeolite B will begin to crystallize. Simultaneously the quantity of faujasite will decrease. Eventually all of the crystalline constituent will be present as sodium zeolite B. The presence of zeolite B may have a detrimental effect on the attrition-resistance of the catalyst product.

During the reaction silica in the microspheres dissolving in the sodium hydroxide reaction liquid to the extent that at the end of the crystallization the mother liquid contains sodium silicate generally having a $\text{SiO}_2/\text{Na}_2\text{O}$ molar ratio of about 2 and the crystallized microspheres have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 0.8 to 1.4/1.

The crystallized microspheres are separated from the mother liquor by screening, filtration or other means. They are usually washed with water before being ion-exchanged to reduce the alkali metal content below 10%, generally below 3% by weight (volatile-free weight basis). Volatile-free weight refers to the weight of a material after it has been calcined to essentially constant weight at 1800°F. Ammonium ions, supplied as ammonium nitrate, chloride or sulphate are suitable although other non-alkali metal cations such as for example magnesium may be used alone or in combination with ammonium ions. The exchanged microspheres are dried and then may be activated by air calcination, steaming or both.

B. Modification of Process in Which Metakaolin is a Reactant

The quantity of faujasite present in the crystallized product may be increased by employing metakaolin in an amount of 1% to 20% of the weight of "Microspheres A" and incorporating such mixture with the sodium hydroxide solution for reaction therewith. The use of a small amount of metakaolin is especially beneficial with regard to the quantity of faujasite that is crystallized when the "Microspheres A" (or a portion thereof) were subjected to temperatures above about 1850°F. during calcination.

In addition to this benefit, the use of metakaolin unexpectedly results in an increase in catalyst hardness, the increase usually being very significant.

Generally the use of metakaolin leads to microspheres having a slightly higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio than products obtained from "Microspheres A" alone. For example, the crystallized microspheres generally have a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in excess of 1.0, e.g., 1.1 when metakaolin is present. When "Microspheres A" are used alone a typical $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 0.97.

In one embodiment of the invention, the metakaolin is introduced as microspheres ("Microspheres B") of essentially the same shape as "Microspheres A." "Microspheres B" may be obtained by calcining one portion of the spray dryer discharge used to obtain "Microspheres A" at a temperature within the range of e.g. 1000°F. to 1500°F., usually about 1350°F., for a time sufficient to remove water and convert any hydrated kaolin to metakaolin. The two batches of microspheres may then be combined in appropriate proportions, described below, and the mixture employed with a suitable caustic solution to form the zeolitic molecular sieve composite.

Alternatively, the calcined microspheres may be obtained from different slurries of clay material. For example, the metakaolin-containing microspheres may be obtained by spray drying a slurry containing raw (hydrated) kaolin and metakaolin and calcining the microspheres at 1350°F. for 2 hours. These microspheres may then be employed, by way of example, with microspheres obtained by spray drying a deflocculated slip consisting of hydrated clay as the sole clay material, calcining the resulting microspheres at about 1900°F. for 2 hours or under other conditions of temperature and time until all of the hydrated kaolin undergoes or passes through the exotherm. Similar microspheres are obtained by employing such calcination conditions (1900°F for 2 hours) with spray dried microspheres consisting essentially of hydrated kaolin, metakaolin, and calcined kaolin that has passed through or has undergone the exotherm or a mixture of meta-

kaolin with calcined kaolin that has passed through or undergone the exotherm. When using these mixtures, sufficient hydrated kaolin clay, preferably at least 50% by weight of the clay mixture, should be used to obtain a hard product.

The metakaolin can be charged to the caustic solution before, after or simultaneously with the addition of "Microspheres A." When metakaolin is charged as a powder, any powder residue should be separated from the microspheres. This may be accomplished when the mother liquid is decanted or otherwise removed from the crystallized microspheres.

Recommended is the use of 1 to 20 parts by weight "Microspheres B" to 100 parts by weight "Microspheres A+" preferably 1 to 15 parts "Microspheres B" to 100 parts by weight "Microspheres A." A low ratio of metakaolin to calcined kaolin clay that has undergone the exotherm favors the crystallization of zeolite Y. Zeolite X is obtained as the ratio is increased. When too much metakaolin is present, the desired crystalline product may not be obtained even when the hydrothermal treatment is carried out for long periods of time, e.g., 48 hours or more. On the other hand, when too little metakaolin is present in the reaction liquid, the quantity of zeolite that crystallizes may be less than desired. This is especially true if the calcined clay in the other microspheres has passed through the characteristic kaolin exotherm.

In spite of the fact that the product is obtained from a heterogeneous mixture of microspheres, it may be obtained virtually free from undesirable mixtures of zeolites. This result was generally contrary to expectations. It would have been reasonable to anticipate that the microspheres composed of metakaolin would react with the aqueous alkaline liquid to form zeolite A or possibly no zeolite, while the other microspheres would be expected to produce faujasite or no zeolite if they had been overcalcined.

50 C. The Product

The catalyst particles analyze at least 90% combined SiO_2 plus Al_2O_3 by weight (volatile-free basis), the Al_2O_3 content usually being from 50% to 65% and the SiO_2 being from 30% to 50% by weight. The balance of the particles is alkali metal oxide (generally Na_2O) up to 10% by weight, preferably less than 3% and advantageously less than 1% by weight and impurities such as TiO_2 which may be indigenous in the clay. The particles are readily distinguished from the other catalysts, including zeolitic catalyst, by the fact that the Al_2O_3 content and the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio are unusually high. Other zeolitic catalysts contain ap-

preciably less than 50% Al_2O_3 . The percentage faujasite in the catalyst ranges from 1% to 70% (as determined by X-ray diffraction). Generally from 10% to 50% faujasite is preferred. Preferably, the faujasite has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio above 4.0 as determined by X-ray diffraction.)

Representative products have a pore value of 0.5 cc./gm. and a bulk density within the range of 0.7 to 0.9 g./cc.

All X-ray diffraction data mentioned herein refer to values obtained by the procedure and with the equipment described in U. S. Specification No. 3,391,994. The percentage of zeolite Y refers to values obtained from X-ray diffraction data using calculations described in said patent. The crystalline zeolite referred to as "zeolite B" was identified by a peak of maximum intensity of $28.2^\circ 2\theta$. Because a reference sample of zeolite B was not available for comparison, the relative portion of zeolite B present was estimated from the intensity of $27.1^\circ 2\theta$ peak for a reference sample of zeolite Y (assumed to be 100% zeolite Y). Zeolite B is described in U. S. Specification No. 3,008,803. According to some authorities, this zeolite is the same as the zeolite known as "Na-P." (See an article by A. M. Taylor et al, "Zeolite Studies IV," THE AMERICAN MINERALOGIST, Vol. 49, May-June 1964, pages 656 to 682.)

EXAMPLE I

A zeolitic molecular sieve was produced, in accordance with this invention, by the following procedure.

Three hundred and seventy-eight parts by weight of powdered hydrated Georgia kaolin clay was blended with 126 parts by weight of Calcined Clay A, 27 parts by weight of Calcined Clay B, 28.0 parts by weight of sodium silicate solution and 436 parts by weight distilled water. Calcined Clay B was a commercial metakaolin pigment obtained by thermally dehydrating high purity kaolin clay under conditions such that the clay undergoes an endothermic reaction associated with the loss of chemically held water but does not pass through the kaolin exotherm. Calcined Clay A was also a commercial calcined clay pigment and is produced by calcination at higher temperatures than used to prepare metakaolin; the clay undergoes the exothermic reaction in the preparation of this pigment. The hydrated kaolin clay was a fine size fraction of water-washed, low iron kaolin clay. The hydrated and calcined clays had a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 2. The sodium silicate that was used contained 38% solids and had a $\text{Na}_2\text{O}/\text{SiO}_2$ weight ratio of 1:3.2.

The ingredients were thoroughly mixed with a "Lightnin' Mixer," (Lightnin' is a

registered trade Mark) producing a fluid slip containing 56% solids and having a density of 1.5 kg./l.

The slip was spray dried in 5 × 5 ft. gas-fired spray dryer using an atomizer wheel speed of 15,760 r.p.m. Air inlet and outlet temperatures were approximately 1100°F. and 450°F., respectively.

The minus 60 mesh (Tyler) fraction of the microspheres was calcined in a muffle furnace at 1800°F. for 2 hours to remove chemically bonded water from the raw clay and to cause the raw clay and Calcined Clay B to undergo the kaolin exotherm. Calcined Clay A had already been dehydrated and had undergone the exotherm.

Sodium hydroxide pellets (23.6 gm.) were dissolved in 144 ml. of distilled water. After the resulting 14% solution had cooled to about 105°F., 100 gm. of the microspheres were slowly added to the caustic solution in a 3-neck round bottom flask. The flask was fitted with a thermometer and a water-cooled condenser through which an agitator extended with the impeller near the base of the flask. The fluid mixture was maintained at 100°F. ± 20°F. for 24 hours while the agitator was in operation. After 22 hours of mixing at 100°F., the temperature was raised to 180°F. and maintained at that temperature while agitation was continued. Samples were periodically removed from the flask with a pipette. The samples were filtered in Buchner funnels and washed with distilled water and dried.

The sample that had been crystallized by heating at 180°F. for 30 hours contained 16.7% sodium zeolite Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 5.0. A trace of zeolite B (estimated at 2%) was also present.

The crystallized microspheres were exchanged by percolation in a 6½" chromatography column with a 1N aqueous solution of ammonium nitrate. The ratio of NH_4^+ in solution per equivalent of Na^+ in the microspheres was about 1.8. After the exchange, the product was washed with distilled water to remove entrained exchange solution. The ion-exchanged microspheres were dried at 200°F. for 18 hours.

A sample of 100-270 mesh (Tyler) microspheres that had been ion-exchanged with ammonium nitrate was activated by calcination in a muffle furnace at 1100°F. for 4 hours.

The attrition-resistance of the 200-270 mesh fraction of the calcined catalyst was measured by the following procedure.

A volume of the heat-treated catalyst (0.661 cc.) and 0.5 g. of 14/20 mesh (U. S. Standard Sieve) silica sand were placed in a 2 cc. vial of a Wig-L-Bug grinding mill and the mill was operated for 5 seconds.

(The Wig-L-Bug grinding mill is a product

of Spex Industries and is described in Catalog No. 5000 of that company.) The sample was then screened and the percentage of minus 325 mesh (Tyler) material was reported as the percent weight loss.

The test was repeated in 5 second increments on the plus 325 mesh (Tyler) portions of the remainder of the sample. A plot of percent weight loss vs. time was obtained. The slope of curve at 20% loss was designated the "attrition rate."

The attrition rate for the experimental catalyst was 1½-2%/sec., which rate is comparable to that of the most attrition resistant zeolitic fluid catalyst commercially available.

EXAMPLE II

The procedure of Example I was carried out on a larger scale. Analysis of intermediates, mother liquid and the catalyst product were made.

After crystallization for 26½ hours at about 180°F., the product contained 22.6% sodium zeolite Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 4.53. The dried intermediate had a L.O.I. (at 1800°F) of 26.98% and had the following analysis (volatile-free weight basis): Na_2O , 6.61%; Al_2O_3 , 56.64%; SiO_2 , 32.94%; TiO_2 , 2.53%; Fe_2O_3 , 0.67%.

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of this product was therefore about 1/1. Since the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the calcined microspheres was about 2/1, about half of the silica in the microspheres had been extracted and passed into the mother liquor during the preparation of the intermediate. This was confirmed by an analysis of the mother liquor which was found to have a Na_2O concentration of 86 g./l., Al_2O_3 concentration of 1.66 g./l. and SiO_2 concentration of 172 g./l.

After ion exchange the product contained (volatile-free weight basis): 1.02% Na_2O by weight; SiO_2 , 35.10%; Al_2O_3 , 60.35%; Fe_2O_3 , 0.68%; TiO_2 , 2.62%.

The cracking catalyst obtained by calcining the ammonium exchanged microspheres had a bulk density of 0.695 kg./l., an attrition rate of 2.6%/sec. and had outstanding activity and selectivity when tested by the CAT-D cracking test.

Thus, microspheres of outstanding hardness and desirable composition for catalytic cracking purposes were inexpensively obtained from microspheres composed of calcined kaolin clay.

EXAMPLE III

The following tests were carried out to illustrate the preparation of fluid catalysts, in accordance with this invention, by spray drying a slurry consisting of hydrated clay as the sole clay material, calcining portions of the microspheres at different tem-

peratures, and reacting mixtures of the resulting calcined microspheres in aqueous sodium hydroxide solution.

- 5 An aqueous slurry of a fine size uncalcined No. 1 paper coating grade of hydrated kaolin clay was deflocculated with tetrasodium pyrophosphate in amount of about 0.3% of the weight of the clay. The slurry was spray dried as in Example I. One portion of the microspheres was calcined in a muffle furnace at 1800°F. for 2 hours ("Microspheres A"). Another portion was separately calcined in the muffle furnace at 1350°F. for 2 hours ("Microspheres B").
- 15 A part of microspheres calcined at 1350°F. was blended with microspheres calcined at 1800°F. in proportion of 10 parts by weight to 90 parts by weight, respectively. The mixture (150 g.) was gradually charged to 220 ml. of a 16.7% (w/w) solution of sodium hydroxide solution and held at 100°F. \pm 20°F. for 16 hours while the mixture was being agitated. The procedures and equipment described in Example I were used. The temperature was increased to 180°F. and agitation was continued while the temperature was maintained at 180°F. for 30 hours.

- 20 The procedure was repeated using 150 g. of microspheres calcined at 1800°F. as the sole calcined microspheres and 220 ml. of the 16.7% sodium hydroxide solution. Reaction at 100°F. was for 14 hours and at 180°F. for 10 hours.

- 35 In all reaction mixtures the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ molar ratio was 0.74/1.

- After crystallization, the microspheres were separated from the mother liquor, washed, ion-exchanged with 1N NH_4NO_3 solution and dried. The products were analyzed for chemical composition, zeolite content and zeolite compositions. Samples were calcined at 1100°F. and tested for attrition resistance (hardness) by the "Wig-L-Bug" test described above. Results are summarized in Table I.

TABLE I
PROPERTIES OF CRYSTALLINE FAUJASITE FLUID CATALYSTS

Reactants	Product				
	NaOH Soln.	Zeolite, %	$\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of Zeolite Y	Chemical Analysis, % *	
Source of SiO_2 + Al_2O_3				Al_2O_3	SiO_2
Microspheres A	16.7%	24% Y 8% B	4.73	62	33
Microspheres A & B	16.7%	40% Y 0% B	4.30	59	36
* volatile-free weight basis				Na_2O	Hardness % per sec.
				<1	1.00
				0.83	0.53

Thus high alumina content, zeolitic catalysts having outstanding attrition-resistance were obtained from single microspheres or mixture of microspheres. Products obtained from the latter were exceptionally hard.

EXAMPLE IV

This example demonstrates the outstanding properties of a cracking catalyst of the present invention.

5 The catalyst was obtained as follows. Calcined microspherical preforms were obtained by forming a 60% solids slip of a fine size fraction of high purity hydrated clay, the slip containing tetrasodium pyrophosphate as a deflocculating agent in 10 amount of 0.3% based on the clay weight. The slip was spray dried to produce microspheres. The microspheres were calcined at about 1800°F. in a muffle furnace for 2 15 hours. After the microspheres had cooled they were gradually added to a 15.0% (w/w) solution of sodium hydroxide, following which a commercial powdered metakaolin pigment was incorporated in amount of 5% 20 based on the weight of the microspheres. The flask containing the reactants was closed with a seal provided with a vent. While the flask was gently shaken, it was immersed in a 100°F. water bath and main- 25 tained in the bath for 12 hours. The temperature of the bath was then increased to 180°F. and, while the flask was shaken, the flask was maintained in the 180°F. bath for 12 hours. The contents of the flask were 30 filtered, washed, exchanged with 1N NH_4NO_3 solution to a Na_2O content of 0.79% and dried.

The ion-exchanged product contained 31.6% zeolite Y having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole 35 ratio of 4.24. Average particle size was 49 microns.

A sample of the ion-exchanged microspheres was dried at 400°F. for 2 hours and then calcined at 1500°F. for 1 hours. Bulk 40 density was 0.89 g./cc. and pore volume was 0.52 cc./g. Hardness by the Wig-L-Bug test was 0.60%/sec.

Another sample of dried ion-exchanged microspheres was activated by heating at 45 1350°F. for 4 hours in an atmosphere of 100% steam. Catalytic properties were tested by the "CAT-D" procedure at a liquid hourly space velocity (LHSV) of 3.0.

To test the thermal stability, a portion of 50 the steamed microspheres was calcined at 1500°F. for 4 hours in 100% steam and then tested by the "CAT-D" method. Results are summarized in Table II.

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TABLE II			
CATALYTIC PROPERTIES OF			
ZEOLITIC CRACKING CATALYST			
Heat Treatment	1350°F./4 hr. +	1350°F./4 hr.	1500°F./4 hr.
(steam)	1350°F./4 hr.		
60 % Zeolite Y	18.8		not tested
Gasoline, Vol. %	60.2		66.4
Coke, Wt. %	6.4		2.1
Gas, Wt. %	25.8		14.8
Gas Gravity	1.64		1.63
65 Conversion, Wt. %	83.1		72.9

Data in Table II show that the catalyst had high selectivity towards gasoline, low coking properties and excellent stability towards high temperature steam.

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WHAT WE CLAIM IS:—

1. A cracking catalyst in the form of attrition-resistant microspheres comprising ion-exchanged synthetic crystalline faujasite 75 and the porous amorphous silica-alumina residue of calcined kaolin clay obtained when the sodium form of faujasite was crystallized in situ by hydrothermal treatment with agitation at 150°-200°F of a suspen- 80 sion in a dilute sodium hydroxide solution of amorphous silica-alumina microspheres comprising calcined kaolin clay, said calcined clay having undergone the kaolin exo- therm during calcination.

2. A cracking catalyst in the form of 85 attrition-resistant microspheres containing ion-exchanged crystalline faujasite and an amorphous alumina-silica residue of alkali metal hydroxide-leached calcined kaolin clay, said microsphere analyzing (on a vola- 90 tile-free weight basis) at least 90% combined $\text{SiO}_2 + \text{Al}_2\text{O}_3$ in a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio within the range of 0.8 to 1.4/1.

3. The catalyst according to claim 2 fur- 95 ther characterized by analyzing (on a volatile-free weight basis) less than 3% sodium oxide.

4. The catalyst according to claims 2 or 3 analyzing (on a volatile-free weight basis) 100 less than 1% Na_2O , from 30% to 50% SiO_2 and from 50% to 65% Al_2O_3 , the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of the faujasite constituent being in excess of 4.0.

5. The catalyst according to claim 1 105 wherein the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio is about 1, said catalyst having been prepared from kaolin clay previously calcined at 1600°F to 2200°F.

6. The catalyst according to any of the preceding claims comprising 10-50% by 110 weight of said faujasite.

7. The catalyst according to any of the preceding claims in the NH_4^+ -exchanged form.

8. The catalyst according to claim 1 115 substantially as described herein.

9. The catalyst according to claim 1 substantially as described herein with refer- 120 ence to any of the Examples.

10. A process for preparing the catalyst 125 of claims 1 or 4 which comprises spray drying a slurry in water of hydrated kaolin clay or a mixture of hydrated and calcined kaolin clay to form microspheres, calcining the microspheres until the hydrated kaolin clay is dehydrated and the microspheres at least partially undergo the kaolin exotherm, suspending said microspheres in an aqueous solution of an alkali metal hydroxide, main- 130 taining said microspheres in said aqueous

- solution at a temperature of 65° to 130°F, subsequently agitating said microspheres in said solution at a temperature of 150° to 200°F until hydrated alkali metal faujasite crystals form in said microspheres and silica is leached therefrom, separating the microspheres from said aqueous solution and ion-exchanging said microspheres to reduce the alkali metal content thereof.
11. The process of claim 10 wherein said alkali metal is sodium.
12. A process for the preparation of a faujasite-containing cracking catalyst according to claims 1 or 4 which comprise spray drying an aqueous slurry of kaolin clay at least 50% by weight of which is hydrated, thereby forming small essentially spherical particles, calcining said particles until any hydrated kaolin clay is dehydrated and the particles undergo the exothermic reaction which is characteristic of kaolin clay, incorporating the calcined particles with alkali metal hydroxide solution to form a fluid slurry, maintaining said fluid slurry at a temperature of 65° to 130°F, subsequently agitating said spherical particles at a temperature of 150° to 200°F and maintaining sufficient water to keep the slurry fluid until silica is extracted from the particles and crystalline alkali metal faujasite is present in the particles, separating the particles from the mother liquid containing dissolved alkali metal silicate, and ion-exchanging the crystallized particles to reduce the alkali metal content.
13. The process of claim 12 wherein said alkali metal hydroxide solution is a sodium hydroxide solution of 12% to 22% by weight concentration.
14. The process of claim 13 wherein the concentration of said sodium hydroxide is 13-15% by weight.
15. The process of any of claims 10-14 wherein metakaolin is also incorporated into the alkali metal hydroxide solution.
16. The process of claim 15 wherein the metakaolin is in the form of small essentially spherical particles and is present in an amount of from 1 to 20% by weight of the said calcined kaolin.
17. A process for the preparation of a catalyst according to claim 1 by hydrothermal treatment without dehydration of an aqueous mixture of sodium hydroxide solution, metakaolin and calcined kaolin that has undergone the kaolin exotherm, comprising reacting metakaolin in the form of calcined coherent first microspheres substantially free from hydrated kaolin clay and calcined kaolin clay that has undergone the exotherm in the form of calcined second microspheres substantially free from metakaolin and hydrated kaolin clay, with sufficient sodium hydroxide solution to form a fluid slurry, and carrying out hydrothermal treatment by maintaining said fluid slurry at a temperature of 65° to 130°F, subsequently heating at a temperature of 150° to 200°F while agitating said fluid slurry sufficiently to keep the microspheres in suspension, and separating the microspheres containing crystalline sodium faujasite-type zeolite and amorphous alumina-silica from the aqueous phase of the slurry.
18. The process of claim 17 wherein said hydrothermal treatment is terminated after the maximum amount of synthetic faujasite has crystallized.
19. The process of claims 17 or 18 wherein said microspheres containing metakaolin substantially free from hydrated kaolin clay are obtained by spray drying a slurry comprising water, a clay material selected from hydrated kaolin clay and mixtures of hydrated kaolin clay and calcined kaolin clay, and calcining the resulting microspheres until the hydrated kaolin is converted to metakaolin.
20. The process of any of claims 10-16 or 19 wherein said slurry from which the microspheres are formed also contains a clay deflocculating agent.
21. The process of any of claims 17-20 wherein said first and second calcined microspheres are obtained by calcination of the same uncalcined microspheres, said uncalcined microspheres being obtained by forming a slurry comprising water, hydrated kaolin clay and a deflocculating agent and spray drying said slurry to form microspheres, calcining a portion of said microspheres until the hydrated clay is converted to metakaolin and calcining another portion of said microspheres until the hydrated kaolin clay undergoes or passes through the characteristic exotherm.
22. The process of any of claims 10-21 wherein the maintenance of the solution at 65° to 130°F is carried out while the microspheres are agitated.
23. The process of claim 10, substantially as described herein and as illustrated with reference to any of the Examples.
24. The catalyst product of the process claimed in any of claims 10-23.
25. A method for cracking a hydrocarbon charge which comprises contacting said charge under catalytic cracking conditions with a catalyst according to any of claims 1-9 or 24.

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(54) **METHOD OF PRODUCTION OF SYNTHETIC ZEOLITE OF TYPE Y**

(57) Abstract:

FIELD: inorganic chemistry, sorbents.
SUBSTANCE: invention relates to production of granulated synthetic zeolite of type Y no containing a binding substance. Natural clay mineral kaolin as the parent material taken in the amount 70-85% of kaolin total mass is subjected for calcination at 700-900 C and treated with sulfuric acid. Insoluble precipitate containing silicon dioxide is washed out with water, mixed with kaolin remained part to provide the final ratio SiO_2 :

Al_2O_3 = (10-12):1 and carbon-containing addition (activated carbon, polyethylene, polypropylene or polystyrene). Water is added to a mixture to form the homogeneous plastic mass and the latter is formed to make granules. Then thermal activation, cooling and crystallization are carried out. The prepared adsorbent can be used in chemical and petroleum chemical industry as a catalyst. EFFECT: high adsorption and strength indices of zeolite. 1 tbl, 4 ex

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